Analytical Chemistry Laboratory

Highlights for October through December 2000

The Analytical Chemistry Laboratory (ACL) provides analytical chemistry services and technical support for a variety of programs at ANL, works collaboratively with programs, and conducts independent research in analytical chemistry. For more information on any of these highlights, call one of the individuals listed with the highlight or the ACL Office at 630-252-4473.

Information about the ACL is available through its World Wide Web home page at http://www.cmt.anl.gov/acl/acl.htm. Topics available from this home page include:

✓ Advice on how to submit samples
✓ Major technical specialties of the ACL staff
✓ ACL Quarterly Highlights since October 1994
✓ ACL Annual Reports for FY 1996 through 1999
✓ List of all published ANL/ACL technical reports

David W. Green, Manager

Lithium Aluminate Methodology Transfer to a Commercial Laboratory (A. M. Essling, F. P. Smith, S. J. Lopykinski, and D. G. Graczyk)

A key objective in ACL's efforts to develop modern, efficient methods for chemical analysis of lithium aluminate is their transfer to a commercial analytical laboratory that would use them to support production-scale manufacture of $LiAlO_2$ ceramics. The program at Pacific Northwest National Laboratory sponsoring ACL in this effort recently contracted a commercial laboratory to implement our procedures and establish qualifications to use them for the program's work. To initiate the transfer, we provided detailed operating procedures and information about equipment so that the laboratory could become familiar with the methods and set up their facilities. Two procedures, one for determining carbon impurity in $LiAlO_2$ and one for the microwave-accelerated dissolution of ceramic samples, have been successfully implemented in the commercial facility. Transfer of other procedures, which require special equipment or more sophisticated operations, is progressing. At an appropriate time, ACL will host an information exchange meeting at ANL where analysts from the commercial laboratory will have an opportunity to view selected operations as performed in the ACL and to resolve questions they might have about specific operations. By working closely with the commercial laboratory as they implement these methods, ACL expects to help the parent program realize substantial returns on its investment for methods development.

Performance Demonstration Program for Analysis of Simulated Headspace Gases for the Waste Isolation Pilot Plant Project (A. S. Boparai, D. V. Applegate, and M. J. Kalensky)

The Waste Isolation Pilot Plant (WIPP) is a DOE installation located in southeastern New Mexico. The WIPP is designed to permanently dispose of transuranic (TRU) radioactive waste left from the research and production of nuclear weapons at the various DOE sites. The WIPP site consists of large interconnecting rooms hollowed out of a salt vein approximately 600 m underground. The WIPP began to receive waste on March 26, 1999. Over the next 35 years, WIPP is expected to receive about 37,000 shipments of waste. Before being shipped to the site, these wastes must be characterized to identify the presence of any hazardous materials in addition to the radioactivity.

Among other characterizations of waste destined for WIPP, analysis of headspace gas for specified volatile organic compounds is required. The National TRU Program Office of the Carlsbad Area Office of DOE has established a performance demonstration program (PDP) for laboratories that will participate in the analysis of headspace gas to be shipped to the WIPP site. The Carlsbad Field Office grants approval to laboratories for analysis of real headspace gases that are successful in analyzing blind audit samples of simulated headspace gases. In support of this effort, the ACL prepares, analyzes, and distributes sets of samples for the headspace gas PDP. Each set contains low, high, special, and duplicate mixtures of analytes.

During the first quarter of FY2001, the ACL performed tasks necessary for sending out the set of samples for Cycle 15A scheduled for February 7, 2001. At present, eleven sets consisting of five 6-L SUMMA canisters are scheduled to be prepared. Unlike previous samples, all of the canisters will be prepared at 6 psi, since none of the participants is using Fourier transform infrared spectroscopy (which requires 30 psi) for determination of analytes.

Acid Matrix Effects in High-Precision Measurement of Lithium and Aluminum (D. G. Graczyk, S. J. Lopykinski, and A. M. Essling)

The ACL is continuing investigation of modern, efficient methods for chemical analysis of lithium aluminate ceramic materials, including a novel inductively coupled plasma-atomic emission spectrometry (ICP-AES) method for determining lithium and aluminum. We had previously found that the ICP-AES method required (1) operating conditions that minimized interelement matrix effects, which cause nonlinear response when the Li:Al ratio varies in standards or samples, and (2) accounting for differences in the emission sensitivity of the two lithium isotopes, ^{6}Li and ^{7}Li. In the course of efforts to recover from an instrument malfunction that required replacing the load coil in the ICP system, we discovered that the method can also be sensitive to seemingly small differences in the acid composition of the solutions that are analyzed. After replacing the load coil and seeking to establish plasma conditions comparable to those previously used, we noted a shift in values for the lithium-to-aluminum ratio measured with a control material that we were working to characterize. The shift amounted to as much as 0.7% of the measured ratio and varied with different operating conditions by several tenths of a percent. Results for check standards did not show the shift. The samples differed from the standards in some way. On further study, we realized that the standards and samples were not perfectly matrix-matched since the samples contained HF at 35 mg/L and were 2.5% in HCl rather than 2%. By analyzing standard solutions with HF and HCl added, we determined that the addition of even this small amount of HF enhanced the lithium signal and suppressed the aluminum signal by an amount that varied from run to run, as observed with the control materials. Changes in the HCl content had only minor effects, as did variations in HF near the sample concentration.

These observations were reassuring because they demonstrated that perfect matching of the acid matrix is not necessary, although the small addition of HF must not be ignored. The procedure for precision ICP was modified to require HF in standards used for samples containing HF. In this way, the acid matrix affects samples and standards in the same way and provides a robust calibration. The identification of this acid matrix effect is important because it represents a significant potential source of bias in the method and is not readily apparent in data obtained under uniform conditions. The existence of such a bias source underscores the importance of having a well-characterized control material available for use in commercial application of the ICP-AES method.

Technical Support for National Analytical Management Program (W. E. Streets)

The ACL is supporting the National Analytical Management Program (NAMP) in the development of centralized information systems that will allow DOE Complex personnel to share pertinent information to promote quality initiatives administered by the Office of Environmental Management (EM). The NAMP Laboratory Informational Network (NAMPnet) provides a single web-based point for users to input and access information about EM contacts at the various sites, costs of analyses, laboratory contracts, audits, and participation in, and assessment of, performance in national performance evaluation programs. Included within NAMPnet are *The U.S. Department of Energy Methods Compendium*, a web-based document containing methods derived from procedures used at DOE sites for analyzing radioactive and mixed waste samples, and the Integrated Performance Evaluation Program (IPEP), which uses information from existing national performance evaluation programs as a cost-effective way to monitor analytical laboratory performance. Much of the work with databases is done with the assistance of the CMT Computer Applications, Network, and Security Group (J. Copple, T. Scandora, J. Kulaga, and R. Krol).

We have linked the NAMP administrative database to the IPEP database, which has made report production simpler. We generated single-study reports for all laboratories in the database for 25 studies in DOE's Quality Assessment Program (QAP), 4 studies in the EPA Water Supply Program, and 5 studies in the EPA Water Pollution Program. For the QAP studies, we generated roll-up reports tailored to each of nine DOE Operations Offices.

We transferred a copy of a database containing commercial laboratory capabilities and audit information to ANL. This database came from the Supplier Quality Information Group, which has developed a formal system to share information about vendors contracted by DOE.

We have also collected additional data from the national performance evaluation programs into the IPEP database.

The ACL provides technical and advisory support to NAMP for other tasks as requested. For example, we

are advising the interagency Methods and Data Comparability Board on the design and development of the National Environmental Methods Index, a web-based database.

Improvements to Microwave-Accelerated Acid Dissolution of Lithium Aluminate (A. M. Essling and D. G. Graczyk)

Previously, we described a method for dissolving lithium aluminate with a microwave-heated sample digestion system. The ACL had established conditions for dependable, complete dissolution of lithium aluminate ceramics with the microwave system and had demonstrated a standard operating procedure for the process. This procedure involved placing a 0.3-g sample in a closed-vessel system with 30 mL of 6 M hydrochloric acid and 0.2 mL of HF, and heating the solution at 240°C for 60 min. We found the amount of HF included in the mixture to be important: if too little was used, then some impurity elements were not dissolved; if too much was used, insoluble aluminum fluoride formed.

Recently, the microwave manufacturer upgraded its microwave system and introduced a new vessel design for high-temperature, high-pressure operation. After our system was converted to the new configuration, we began encountering problems with vessel failures that impaired sample throughput and reduced the attractiveness of the method. Through collaboration with the system manufacturer and limited experimentation, the problem was overcome by reducing the operating temperature from 240 to 230°C. In addition, the system manufacturer determined that overpressure protection was improved under the conditions of our method if the relief system used a different style of fittings and burst membranes. With the lower temperature and new fittings, vessel failures were virtually eliminated with no detriment to the effectiveness of the dissolution. The solution obtained is suitable for use in spectroscopic determination of lithium isotopes, lithium and aluminum content, and cation impurities.

Publications

"Removal of Lithium Antimonide from Radioactive Glovebox." L. Leibowitz, S. M. McDeavitt, D. G. Graczyk, and F. P. Smith, *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, **Vol. 4**, No. 4, October 2000.

"The Art of Being Uncomfortable," D. W. Green, *Managing the Modern Laboratory*, **5**(1), 4A-6A (2000).

"Forum on Communicating with Clients," D. W. Green, *Managing the Modern Laboratory*, **5**(1), 16A-19A (2000).

The "Request for Technical Services" Form (ANL-80) is available on line through the ANL forms page: http://www.ipd.anl.gov/aim/forms

If you submit samples regularly, you can save a copy to avoid starting from scratch with this form for the next set of samples. The form can be sent electronically to the ACL analyst or group leader, but it should be received from the person who normally signs the "Cost Code Authorization" box on the hard copy version. There can be some advantage to sending a printed hard copy of the form with the samples to be analyzed.